

NEW CONCEPTS IN
POLYMER SCIENCE

Ecological Aspects of Polymer Flame Retardancy

S.M. Lomakin and G.E. Zaikov



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Ecological Aspects of Polymer Flame Retardancy

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Foreword

"There are two possibilities - either mankind will make less smoke to be on Earth or the smoke will make fewer men to live."

G. Barton

"Our globe resembles a car, running alone in a space with the exhaust pipe channeled into the passengers' compartment. The more force we apply to the accelerator, the higher the probability that we poison the driver and the passengers."

Jacques Yves Cousteau

The two sayings given above well define the significance of the problem formulated in the monograph title. One may cite a prophecy about the future made by Leonardo da Vinci, the great artist of the Renaissance period "Devastating wars will always take place on Earth and death will be not a frequent destiny of the fighting sides. These savages will annihilate many trees from the planet's woods with infinite spite and then vent their rage on every living thing to be found around, bringing them pain and destruction, suffering and death. Neither on the ground, nor under it, nor under the water will anything remain untouched or undestroyed. The wind will blow plantless ground all over the world and cover the remains of the creatures that one day made different countries alive with it." One can see, that the creator of the "Mona Lisa (Giaconda)" did not have a very high opinion about the future generations of mankind. Fortunately, it has not happened precisely as he predicted. However, his widespread anxiety about the future and about the probable miscalculations of humankind appear to be correct.

This problem is connected with ecology. The quantity of polymers used by humans has become a measurement of progress. More than 130 million tons of artificial polymers and approximately the same amount of natural polymers are now produced in the world. Together they make up over 250-260 millions of tons. If this quantity is converted to volume, then it gives 240 million cubic meters of polymers per year. These figures may be compared with those for other common industrial materials: there are produced approximately 240 million cubic meters of steel and 14 million cubic meters of nonferrous metals per year.

But this is not all. The dynamics of development are also important. Here we have the following figures: during the period from 1995 to 2010 the volume of polymer production is expected to double while the increase of production of the basic metals is expected to rise only 1.5 times. According to a Russian proverb, humans are increasingly "cutting the branches on which they are sitting". Polymer waste is increasing tremendously. Most countries simply burn them in special furnaces: The result is poisoning of the environment.

Thus it is inevitable that the more humankind uses polymer products, the more accidental fires will result from them. The reduction of polymer flammability thus becomes a major problem of pure and applied chemistry.

According to the president of the American Chemical Society, Professor Gordon Nelson from the Florida Institute of Technology (USA), during accidental fires, about half of the people die not from burns, but from poisoning by products of polymer combustion. These results, with only minor differences in statistical data have been verified by numerous scientists from various countries in the world. Among them it is possible to mention the group of researchers under Dr. Takashi Kashiwagi from the National Institute of Standards and Technology; Professors Eli Pearce, Menachem Lewin and Edward Weil of Brooklyn Polytechnic University (New York); Professor Charles Wilkie of Marquette University (Milwaukee, WI); Professors Giovanni Camino and Luigi Costa of Turin University (Italy); Professors Norman Grassie and Ian McNeil of University of Glasgow (Scotland, UK); Dr. Joseph Green of Research Center of FMC Corp. (Princeton, NJ); Professors. Al. Al. Berlin, R.M. Aseeva, N.A. Khalturinskii of the Institute of Chemical Physics, Russian Academy of Sciences; Professor Richard Horrocks of the Bolton Research Institute (UK); Professor Rene Delobel and Dr. M. Le Bras of University of Lille

(France); Professor William Herbert Starnes of William and Mary College (Williamsburg VA).

So there are two problems:

1. To make non-combustible polymers.
2. If they are flammable, to make sure that they will not produce toxic products and halogen derivatives which poison the environment and destroy the ozone layer of the atmosphere.

These two problems remind us of a Russian proverb: "Do not smoke. Do not throw stubs on a floor." This is a colloquial version of the given problem.



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Preface

We will remind the reader that solid bodies (in particular polymers) are not intrinsically flammable. This has been established since 1920-1930 by scientists of the school of the Nobel Prize laureate, professor Nikolai Semenov and the architects of the Soviet nuclear bomb, Professors Yuli B. Khariton and Jacob B. Zel'dovich. However, the gaseous products of polymer pyrolysis do burn. Hence, the lower is the speed of pyrolysis, the less is the polymer combustibility. The pyrolysis of polymers is the first and most important stage of combustion.

Since polymers were introduced, scientists have created only three basic ways to reduce polymer flammability:

1. To add some chemicals that at high temperatures produce radicals of low-molecular mass and low-activity. For instance, chlorine and bromine derivatives at high temperatures produce Cl and Br atoms of low activity that can terminate the propagation of the radical chain reactions of combustion.
2. To incorporate some additives into a polymer material that can create a coke or other coating onto a polymer body. This layer prevents the processes of heat and a mass transfer. The atmospheric oxygen and the flame are not able to act with any free polymer surface and a combustion process may thus be suppressed.
3. To add the chemical compounds that at high temperatures can evaporate, but retaining a high thermal capacity.

Anyone with average education might suspect that the best of such additives is water with its

large heat capacity. One well known method of reducing flammability is the microcapsulating of water into some polymer composites. Under heating conditions of the polymers, the capsules burst to release the water and to depress combustion. However, there is a big practical problem on the transition from pure to applied chemistry: this is diffusion. Freshly prepared samples of polymers do not burn, but aged specimens burn very well. The reason for this phenomenon is the process of diffusion and evaporation of water through a polymer matrix under condition of storage and use.

So, we have the idea of pyrolysis, as the first stage of the process of burning, and the three basic mechanisms to reduce the flammability of polymer materials. Proceeding from these concepts, the authors of this book present new opportunities of polymer flame retardation with a view to ecological protection. The concern and current interest in this field is based on the negative environmental impact of some industrial flame retardants containing halogens, heavy metals etc. The suggestions herein are definitely some of the first and most important steps in the direction of the future evolution of flame retardants and consideration of general ecology.

Prof. Alexander A. Berlin

Director of the Institute of Chemical Physics

Russian Academy of Sciences

Introduction

Plastics have played an important role in our history. After the invention of celluloid in the 1860s, plastics have demonstrated endless possibilities for application. Since then, plastics have become an integral part of our everyday life.

The interest in flame retarding plastics goes back to the mid nineteenth century with the discovery of highly flammable cellulose nitrate and celluloid. In more recent times, a large volume of conventional plastics, such as phenolics, rigid PVC and melamine resins, possess some flame retardancy. By the 1970s the major flame retardant polymers were the thermosets, namely, unsaturated polyesters and epoxy resins which utilized reactive halogen compounds and alumina hydrate as an additive. There was also a large market for phosphate esters in plasticized PVC, cellulose acetate film, unsaturated polyesters and modified polyphenylene oxide. Alumina trihydrate (ATH) was the largest volume flame retardant added to unsaturated plastics.

Consumption of halogen-containing flame retardant additives in 1970s was much less than that of the other additives. The halogenated flame retardant additives were Dechlorane Plus, a chlorinated acyclic (for polyolefins), tris-(dibromopropyl) phosphate, brominated aromatics, pentabromochloro cyclohexane and hexabromocyclododecane (for polystyrene). The next five years were to see a number of new brominated additives on the market. Also, a number of chlorinated flame retardant compounds were produced under the Dechlorane trade name. The products include a coupled product of two moles of hexachlorocyclopentadiene that contained 78% chlorine, Dechlorane Plus, a Diels-Alder reaction product of cyclooctadiene and hexachlorocyclopentadiene with 65% chlorine, a Diels-Alder product with furan and a product containing both bromine and chlorine with 77% halogen developed for the polystyrene and ABS materials.

In 1985-86, a German study detected brominated dioxins and furans from laboratory pyrolysis at 510-630°C of a brominated diphenyl oxide. The relevance of these pyrolysis studies to the real hazard presented by these flame retardants under actual conditions of use has been questioned.

Germany and Holland have considered a ban or curtailed use of brominated diphenyl oxide flame retardants because of the potential formation of highly toxic and potentially carcinogenic brominated furans and dioxins during combustion. The issue spread to other parts of Europe where regulations were proposed to restrict their use. Nevertheless, demand for brominated flame retardants, including decabromo- and pentabromodiphenyl oxides, continues to be strong and is growing.

The Hazards Substance Ordinance in Germany specifies the maximum level of chlorinated dibenzodioxins and furans that can be present in materials marketed in Germany. This has been extended to the brominated compounds. The two largest volume flame retardants - decabromodiphenyl oxide and tetrabromobisphenol A - are said to meet these requirements [1,2].

The International Program for Chemical Safety (IPCS) of the World Health Organization has made several recommendations. Polybrominated diphenyls production (France) and use should be limited because of the concern over high persistency, bioaccumulation and potential adverse effects at low levels. There is limited toxicity data on deca- and octabromodiphenyls. Commercial use should cease unless safety is demonstrated. For the polybrominated diphenyl oxides, a Task Group felt that polybrominated dibenzofurans, and to a lesser extent the dioxins, may be formed. For decabromodiphenyl oxide, appropriate industrial hygiene measures need to be taken and environmental exposure minimized by emission control. Controlled incineration procedures should be instituted. For octabromodiphenyl oxide, the hexa- and lower isomers should be minimized. There is considerable concern over persistence in the environment and the accumulation in organisms, especially, for pentabromodiphenyl oxide.

In September 1994, the US Environmental Protection Agency (EPA) released a final draft of exposure and risk assessment of dioxins and like compounds [3]. This reassessment finds the risks greater than previously thought. Based on this reassessment, a picture emerges that tetrachlorodiphenyl dioxins and related compounds are potent toxicants in animals with the potential to produce a spectrum of effects. Some of these effects may already be occurring in humans at very low levels and some may be resulting in adverse impacts on human health. The EPA also concluded that dioxin should remain classified as a probable human carcinogen. The EPA homed in on one particular industry for regulatory action, namely waste incineration, and laid out plans to cut dioxin emissions drastically over the next few years. The American Industrial

Health Council disagrees with EPA's declaration that dioxin is definitely linked to a lung cancer and soft-tissue sarcoma [4]. Industry scientists have stated that the scientific evidence does not support EPA's conclusions that adverse human health effects can be expected at or near background exposure levels.

There are no regulations proposed or in effect anywhere around the world banning the use of brominated flame retardants. The proposed EU Directive on the brominated diphenyl oxides has been withdrawn. Deca- and tetrabromo bis-phenol A as well as other brominated flame retardants meet the requirements of the German Ordinance regulating dioxin and furan content of products sold in Germany. The European search for a replacement for decabromo diphenyl oxide in HIPS has led to consideration of other bromoaromatics such as Saytex 8010 from Albemarle and a heat-stable chlorinated paraffin from ATOCH EM. The former product is more costly, and the latter, if sufficiently heat stable, lowers the heat distortion under load (HDUL) significantly. Neither approach has been fully accepted.

Polymer producers, compounders and end-product manufacturers have been seeking non-halogen flame retardants and the search has been successful in several polymer systems. Non-halogen flame retardant polycarbonate/ABS blends are now commercial. They contain a triphenyl phosphate or resorcinol diphosphate as the flame retardant. Modified polyphenylene oxide has used phosphate esters as the flame retardant for the past 15-20 years. Red phosphorus is used with glass-reinforced nylon 6,6 in Europe and melamine cyanurate is used in unfilled nylon. Magnesium hydroxide is being used commercially in polyethylene wire and cable. The non-halogen solutions present other problems such as poor properties, difficult processing (high loadings of ATH and magnesium hydroxides), corrosion (red phosphorus) and handling problems (red phosphorus).

Much remains to be solved in complete replacement of ecologically harmful flame retardants. This is a problem for many years. But the final issue is obvious. All efforts should give positive results in the search for new ecologically friendly flame retardants.

From this point of view, this monograph differs from the other books on polymer flammability on the same subject in that we emphasize a general problem of flame retardants' impact on the environment.

The information presented and the ideas developed in the monograph will be of interest to all those concerned with polymer flame retardation with respect to ecological concerns.



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Chapter 1

Some Concepts of Polymer Combustion

The flammability of natural and synthetic polymer materials is determined by the ability of such materials to ignite and spread the combustion process. Combustion is defined as a fast, self-accelerating exothermal redox process that is able to spread in the environment and is accompanied by luminosity and the formation of a flame. Combustion may be of either a chain or a thermal nature, depending on the cause of initiation and development: accumulation of active particles in the system or the liberation of heat.

The combustion of common polymer materials is viewed as a heat-generating process, as in the case of the overwhelming majority of other substances. Initiation of the polymer combustion process is based on the fact that the heat liberated as a result of redox reactions is not able to enter the surrounding atmosphere but heats the reacting system and increases the rate of reaction. The resulting heat then causes self-propagating combustion even after the ignition source has been removed. The phenomenon of a progressive auto-acceleration of a chemical reaction under the effect of liberated heat is called a thermal explosion [5,6].

The specific characteristic of a thermal explosion is the existence of critical conditions for its development. The chemical nature of the fuel and the oxidizing substances differs, as does the mechanism of the combustion reactions. A pronounced relationship between the rate of heat liberation and the temperature is a major factor characterizing the reaction occurring in heat liberation. When the rate of heat input is equal to the rate of heat required to maintain the process plus losses to the surrounding atmosphere, then a steady - state combustion process has been established.

Basically, the oxygen from the air is used as an oxidizing agent in polymer combustion. The reaction between the oxygen and the polymer and the fuel products of polymer degradation and vaporization is dependent on the reagent mixing and diffusion conditions. This is why